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# CHEMICALLY INDUCED IGNITION IN AIRCRAFT AND SPACECRAFT ELECTRICAL CIRCUITRY BY GLYCOL/WATER SOLUTIONS

*by W. R. Downs*

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Houston, Texas*



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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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## ABSTRACT

Electrical circuitry of military aircraft and spacecraft consists, in part, of insulated silver-covered copper wires and components. This circuitry creates a potential flammability hazard when solutions of glycol/water come in contact with either a bare or a defectively insulated wire or component carrying direct current. The hazard arises from chemical reactivity of the silver-covered copper anode in contact with glycol/water solutions. Similar reactivity does not occur with pure copper, nickel-covered copper, or tin-plated copper elements in electric circuits. Some chemical and physical properties of glycol/water fluids are presented, and glycol-induced corrosion of metals and corrosion inhibitors are discussed. A tentative chemical mechanism for the reactions of glycol/water solutions with silver wire carrying direct current is proposed. A means of detecting reaction by use of a transistorized amplitude-modulation receiver is reported, and a means of preventing reaction of glycol/water solutions with silver wires carrying direct current by adding a silver chelating agent to the glycol/water fluid is described.

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GLYCOL/WATER SOLUTIONS

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SUMMARY

Work at the NASA Manned Spacecraft Center following the Apollo-Saturn 204 incident in January 1967 demonstrated that bare or defectively insulated silver-covered copper wires carrying a direct-current potential produced ignition when contacted by glycol/water fluids used in the Apollo environmental control system. Mechanisms of inhibiting glycol/water-induced reactions with metals are discussed with particular reference to the Apollo coolant fluids. Measurements of milliampere current flow during the reaction of glycol/water with silver and utilization of a transistorized amplitude-modulation receiver for detecting radiofrequency emissions are described as a means of locating circuitry defects leading to flammability. Since glycol/water coolant fluids cannot easily be removed from contaminated circuitry, use of a silver chelating agent in the glycol/water coolant to arrest chemical reactivity and thereby minimize the hazard of flammability is proposed.

INTRODUCTION

Since World War II, silver-covered copper wires (Military Specifications MIL-W-7139 and MIL-W-8777) have been used in electrical circuits in military aircraft because of the ease and reliability with which silver can be soldered to produce high-quality electric circuits. It was natural, therefore, to specify silver-covered copper wires in spacecraft construction. Use of silver-covered wires, switches, and disconnects seemed sound, not only because of the ease of joining but also for the protection afforded copper by the resistance of silver to oxidation when high-melting polymers for electrical insulation coverings were extruded over the conductor. Because of occasional bleed-through of copper to the surface of the silver, some aerospace designers specify nickel-covered copper wires instead of silver-covered copper wires. Nickel-covered copper wires are used in the Apollo command module (CM), and silver-covered copper wires are used in the lunar module (LM). The ground-support-equipment wiring and auxiliary wiring are usually insulated, and are pure copper or tin-plated copper wires.

Chemical effects of glycol/water solutions on electrical wire circuitry of aircraft or spacecraft have practical importance in the aerospace industry. This was illustrated by the investigations following the Apollo AS-204 incident in January 1967, when it was observed that defectively insulated spacecraft coaxial silver-covered copper cable carrying 28 volts direct current in a 16.7-psia pure oxygen atmosphere caught fire when glycol/water thermal transport fluids dripped over the cables. In the investigations it was noted that the time required to attain ignition after onset of the glycol/water exposure was an inverse function of the drip rate; that is, the slower the drip rate, the more rapidly ignition occurred. Further observation showed that defectively insulated pure copper cables exposed to glycol/water coolant in oxygen did not produce fire.

An examination of the glycol/water-induced corrosion of metals, of mechanisms for inhibiting corrosion, and of the reasons why silver-covered copper wires reacted differently than copper or nickel-covered wires when exposed to glycol/water solutions therefore seemed appropriate. This paper discusses the use of additive reagents to inhibit reactivity of glycol/water solutions on wire circuitry, gives a tentative explanation for the observed reactivity of silver to glycol/water solutions, and proposes a means of detecting some types of ongoing chemical reactions in wire circuitry before fire ensues.

## MECHANISMS FOR INHIBITING FLUID-METAL REACTIONS

The inhibitor system found superior for the Apollo CM and LM environmental control units is termed "NAA Type II." It contains a pH buffering agent (triethanolamine phosphate, called TEAP) and a copper chelating agent (sodium mercapto benzothiazole, called NACAP) (refs. 1 and 2). The TEAP in NAA Type II has three functions: (1) to pull copper atoms on the surface of the alloy into solution where the chelating agent (NACAP) can react with the copper ions to form an undissociated copper chelate (organometallic complex); (2) to supply phosphate ions to produce a uniform coating of aluminum phosphate over the metal surfaces, thereby protecting the natural oxide coating; and (3) to serve as a phosphate salt buffer for maintaining the pH of the solution close to 7 and preventing wide local excursions of the hydrogen ion concentration.

Other corrosion inhibitors for spacecraft are available, for example, a potassium phosphate-tetraborate mixture known as NAA Type III, anthranilic acid, or boric acid. The use of selective oxidation agents, such as potassium tetraborate, is employed in NAA Type III. The potassium tetraborate, in conjunction with potassium monoacid phosphate, produces a thin tenacious coating of aluminum oxide borate on the metal surfaces, thus preventing corrosion.

The choice of an inhibitor system for glycol/water solutions depends on the metals used in the coolant loop construction of the spacecraft. The Apollo environmental control system utilizes NAA Type II in a eutectic mixture (a eutectic mixture is one

which has the lowest freezing point possible) consisting of 62 percent ethylene glycol and 38 percent water (G/W-1). This mixture carries the trade name of "RS 89-a."<sup>1</sup>

RS 89-a (in bulk quantities) is not a fire hazard in a 15-psia oxygen atmosphere. Its autoignition point has been demonstrated to be somewhere above 450° F in a 15-psia oxygen atmosphere; in air, this point is given at 790° F for RS 89-a and at 750° F for pure ethylene glycol. The flashpoint temperature of RS 89-a is between 230° and 240° F.

### LABORATORY DATA

A series of laboratory experiments was performed at the NASA Manned Spacecraft Center (MSC) to determine the physical properties of RS 89-a and its effects on wire circuitry so that a method could be specified for cleaning contaminated circuit elements.

NASA MSC laboratory distilled water at ambient temperature (23.3° C) has an ion concentration of 0.74 ppm. By contrast, RS 89-a fluid at ambient temperature produces an ion concentration of 243.0 ppm because of the phosphate and sodium ions in the inhibitors.

RS 89-a cannot, within practical time limits, be completely evaporated by vacuum techniques because of the presence of the ions and because of the low vapor pressures of the ethylene glycol and undissociated amines. Excess tertiary amine and its phosphate, on evaporation of solvent, remain as hygroscopic material and are deliquescent. They tend to pull water from the surroundings to produce an electrically conductive, corrosive fluid. The sodium ions present will remain as the salt, sodium mercapto benzothiazole. In any case, the sodium ions, the undissociated alkaline amine, and the ethylene glycol remain when RS 89-a is spilled around electrical cables or on electrical connectors, despite efforts to evaporate the spillage by pulling a vacuum.

Because of the hygroscopic nature of the amine residues and the existence of ions, a corrosive, electrically conductive moist locale is produced, commencing with the admission of air or moist oxygen to the RS 89-a-soaked equipment. The pulling of moisture to RS 89-a-stained regions is time dependent and cumulative. The cleansing of wire circuitry contaminated with glycol/water requires adherence to criteria which are based on the physical properties of the mixture. The criteria are as follows:

1. Removal or dilution of pools of glycol/water solution is imperative, since the solution can feed a firesite.

2. Cleaning liquids (for example, alcohols and Freons) which tend to spread contaminants are harmful.

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<sup>1</sup>RS 89-a is compounded to the following proportions: 566 grams of ethylene glycol, 399.5 grams of distilled water, 14.18 grams of TEAP, and 1.41 grams of NACAP (50-percent solution) for a total of 921.09 grams.

3. Evaporation of contaminants is not possible because of the low vapor pressure of ethylene glycol and the presence of ionic species.

Based on the previously discussed criteria, the use of distilled water is specified for repetitive rinsing and drying of contaminated wire circuitry until the rinse water achieves a low ion content arbitrarily selected at a value not to exceed that of twice the ion concentration of the distilled water.

The NASA MSC observations showed that bare or defectively insulated silver-covered copper wires (carrying a direct-current potential) exposed to glycol/water solutions produced smoke and fire in oxygen or in air. Also, it was found that copper wires or nickel-covered copper wires under conditions of electrical potential and oxygen exposure identical to that of silver-covered wires did not exhibit chemical reactivity to glycol/water solutions and did not produce ignition.<sup>2</sup> The experimentation is described in the following paragraph.

Silver-covered copper wire as used on the LM circuitry was completely stripped of its insulation. Two pieces, each about 5 centimeters long, were taped to cardboard so that approximately a 1-millimeter space separated the two wires. A 22.5-volt dry-cell battery supplied direct-current potential, and the wires were attached to the battery terminals with a direct-current milliammeter in series. RS 89-a solution was dripped slowly into the 1-millimeter space between the wires. Electrolysis commenced at once, and in 4 to 5 seconds a black deposit was observed on the silver wire connected to the positive terminal of the battery. The milliamperage current flow fluctuated between 10 and 80 milliamperes, and the needle of the meter jumped constantly. In a few minutes, copious white smoke and flame ensued. These phenomena occurred whether the reaction was carried out in air or in 100 percent oxygen at 15 psia.

A transistorized amplitude-modulation (AM) receiver placed near the electrolysis started to click and emit static, which, as the electrolysis proceeded, built up to a constant static noise that drowned out all other reception on the receiver. The radio-frequency (rf) disturbance was observed on the receiver when it was held as far away as 3 feet, and the intensity of the noise increased as the receiver was moved toward the reaction site. The application of the AM receiver to detect a reaction between the glycol/water solution and the silver wiring was found to be more convenient than using a milliamperage meter in the circuit. The slower the application of glycol/water solution after the first drop or two, the louder the rf disturbance over the receiver became. Finally, the chemical reactions detected by the AM receiver produced smoke and flame.

Nickel-covered copper wires, pure copper wires, and tin-plated copper wires did not show evidence of chemical reactivity when subjected to a direct-current potential

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<sup>2</sup>D. K. Elliot (ref. 3) reports on so-called wet-wire fires produced from insulated wires of various metal compositions when the wires are exposed to direct current and to aqueous conducting solutions. The work of Elliot discusses a different sort of phenomenon, namely, the formation of metallic dendrites leading to an electrical short, followed by ignition and burning of the wire insulation.



and exposed to the glycol/water solution. In such instances, the solution simply electrolyzed away with mild generation of heat, with no rf radiation emission, and with no tendency to flammability.

To illustrate the previously described phenomena and to compare the reactions of silver-covered and nickel-covered copper wires with the glycol/water solution, two bare wires separated by a sheet of filter paper were connected to a 22.5-volt battery, with a milliamper chart recorder in series in the circuit. When the first drop of glycol/water solution was placed on the filter paper, a current measured in milliamperes was established. Four experiments were performed in air.

The first experiment showed the effect of glycol/water (RS 89-a) solution on nickel-covered copper wires. Current flow was observed for the first few seconds following each drop of glycol because the glycol/water solution was evaporating because of electrolysis during this time. Thereafter, no current flowed until the next drop was made. Six droppings were made over a 45-minute interval; the experiment was then discontinued. There was no smoke, and no ignition resulted.

The second experiment showed the effect of uninhibited glycol/water solution on silver-covered copper wires. Two drops of solution produced ignition in slightly over 7 minutes, with a current flow sustained after the first half minute.

The third experiment showed the effect of NAA Type III inhibited glycol/water solution and of RS 89-a glycol/water fluid on silver-covered copper wires. The first drop of solution in both instances produced ignition in less than 1 minute, with a sustained current flow.

The fourth experiment showed the effect of a low-ion inhibitor (anthranilic acid) in glycol/water solution (G/W-1) on silver-covered copper wires. Current flow started on the first drop and terminated with ignition when the second drop was made at 7 minutes; the behavior was similar to that of the uninhibited glycol/water solution.

The foregoing experimental results were independently confirmed by Boies and Northan (ref. 2). In the current investigation, further laboratory verification was obtained by dripping RS 89-a fluid on defectively insulated coaxial silver-covered copper cable and on nickel-covered copper cable in a 100 percent pure oxygen atmosphere at 15 psia. The chemical reactivity of silver-clad wires was measured by recording the current flow until ignition and subsequent burning of the glycol occurred. Nickel-covered copper wires did not produce heavy current flow between the conductors, and ignition did not ensue.

It makes little difference in reactivity whether the glycol/water fluid is simply ethylene glycol solution in water or if the fluid contains inhibitors such as NAA Type II or Type III. Chemical reaction of silver with glycol/water solution occurs only when the silver is the positive terminal. This signifies that the silver undergoes anodic oxidation, which occurs readily at a 6-volt potential but is barely apparent at a 1.55-volt potential. The latter, therefore, is considered to be the minimum potential at which reactivity commences.

Reaction occurs as soon as glycol/water contacts the current-carrying silver-covered wires, evidencing itself initially by electrolysis between the wires and by the

formation of a black deposit. Steps in the chemical mechanism leading to ignition are shown in figures 1 to 5. These figures are stereoscopic photomicrographs produced from frames of a movie film taken of the reaction resulting when RS 89-a fluid was placed between two silver-covered wires separated by a distance of 1 millimeter and impressed with 22.5 volts of direct current. The action occurred over a span of approximately 1 minute, during which time the current did not exceed 80 milliamperes and the average current was 50 milliamperes. In the figures the upper wire is negative and the lower wire is positive.

Figure 1 shows hydrogen bubbles forming at the negative pole and streamers of brown silver hydroxide issuing from the positive pole. This happened as soon as the current was impressed.

As seen in figure 2, within a few seconds the silver hydroxide conglomerated to black silver oxide. Centers of explosive energy releases are visible in the mass of silver oxide as ethylene glycol commenced to dehydrate.

Figure 3, a view several seconds later than the view in figure 2, shows an extensive region of glycol oxidation (indicated by the intense blue light) accompanying the decomposition of the ethylene glycol, the rearrangement to form ethylene oxide, and the formation of ethylene. Steam and smoke are observed rising from the negative-pole regions.

Figure 4 shows generalized reaction all along the wire surfaces and copious liberation of smoke and steam, indicative of energy releases in excess of the energy drain from the battery. The total power from the battery, if the maximum current rate were maintained for 1 minute, would be 108 joules (approximately 25 gram-calories), most of which would produce silver oxide and hydrogen, as noted in figures 1 and 2.

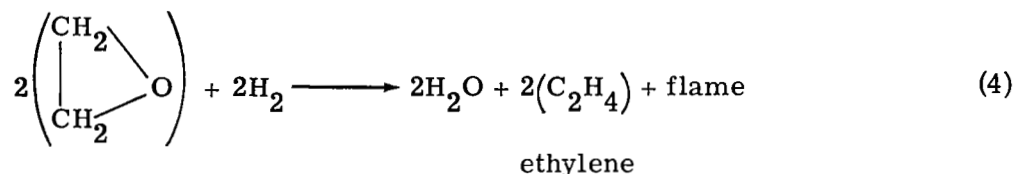
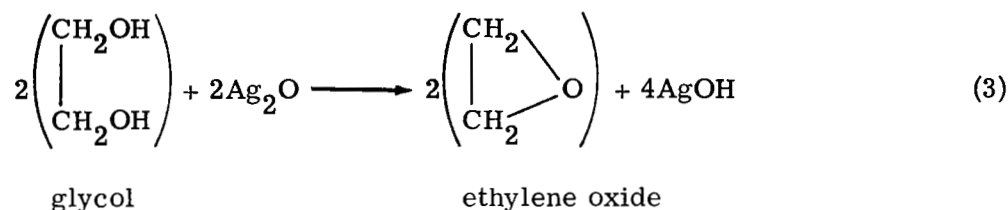
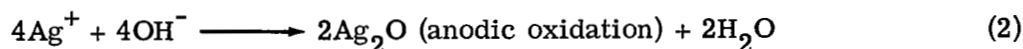
In figure 5, a burst of flame, caused by the reactions of ethylene oxide with hydrogen and of ethylene with air, is visible in the negative-pole region. Another burst is seen on the right side. Analysis showed that the washed-and-dried black deposit contained silver, carbon, oxygen, and nitrogen (ref. 4).

Pure copper wires or nickel-covered copper wires, in contrast to the reaction of the silver-covered copper wires, do not react when exposed to glycol/water solutions, either in air or in pure oxygen atmospheres. On these types of wires, the glycol/water solution evaporates (from the heat of electrolysis) without producing incandescence or sparks. It has been found impossible, even in a 100 percent pure oxygen atmosphere at 15 psia, to produce ignition from nickel-covered or pure copper wires carrying direct-current voltage upon exposure to glycol/water solutions.

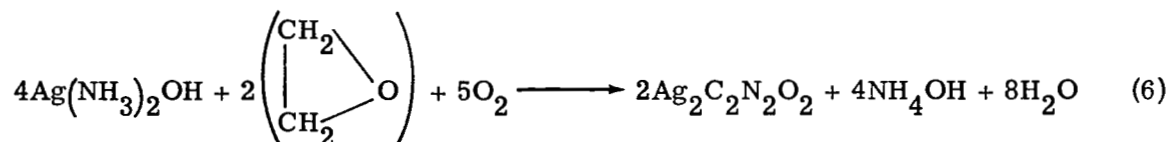
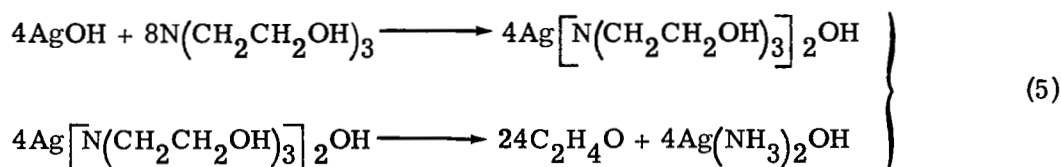
## CHEMISTRY OF OBSERVED PHENOMENA

Laboratory results indicate that silver-covered copper wires impressed with a direct-current potential react chemically with glycol/water solutions. Pure copper or nickel-covered copper wires similarly treated do not react with glycol/water solutions; instead, the solution boils away with some dissolving and plating of the copper. These observations can be explained chemically as follows.

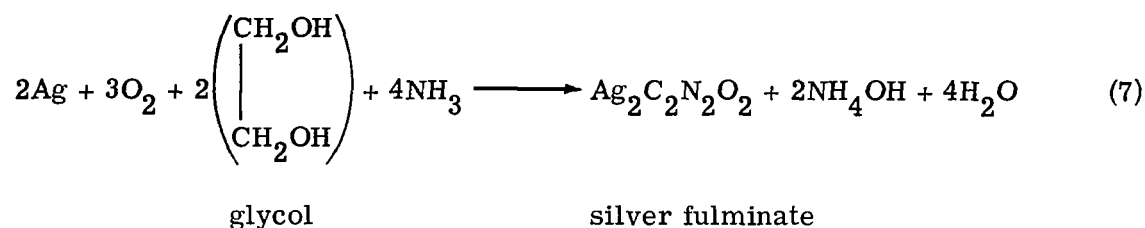
Silver is anodically oxidized to silver oxide ( $\text{Ag}_2\text{O}$ ), which dehydrates glycol to ethylene oxide, which in turn reacts with hydrogen from the electrolysis. These reactions are represented by the following equations:



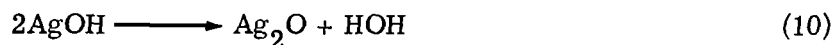
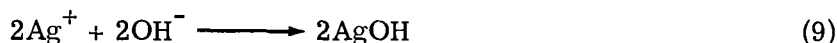
If amines are present (for example, TEAP in RS 89-a), the triethanolamine reacts with silver hydroxide ( $\text{AgOH}$ ) to form silver ammonia hydroxide ( $\text{Ag}(\text{NH}_3)_2\text{OH}$ ), which in turn is oxidized by ethylene oxide and oxygen to yield silver fulminate which is a sensitive detonator. The reactions are as follows:



A complete chemical equation is obtained by adding equations (1) to (6) to yield



The chain-reaction mechanism involving the action of glycol/water solution on silver wire begins with the anodic reactions



The chain-reaction mechanism may be prevented if a silver chelating agent exists in the solution to tie down the  $\text{Ag}^+$  ion before it can form silver oxide. Such a chelating agent is benzotriazole, suggested in reference 2. It has been confirmed experimentally that benzotriazole in concentrations of from 2000 to 5000 ppm in glycol/water solutions inhibits the chemical reactions of silver and glycol under an impressed direct-current potential. No black deposits form on the silver electrode, no rf radiation is detectable on an AM receiver near the reaction site, the reactants do not tend to flame, and the current flow is steady and time decreasing. The interaction of benzotriazole decreases the activity of silver towards glycol/water solutions to a point where the silver-covered copper wires behave similarly to nickel-covered or pure copper wires; namely, a simple electrolysis occurs between the shorted wires which gradually ceases as the solution evaporates. The benzotriazole interaction produces a greenish-white gelatinous precipitate around the silver conductors. This precipitate presumably is an organo-silver chelate hydroxide which removes the silver ion and thereby prevents formation of silver oxide. The current flow between the wires is impeded by the precipitate, and the reaction rates are noticeably slowed. The chain-reaction mechanism leading to flammability is interrupted and prevented.

## CONCLUSIONS

Work at the NASA Manned Spacecraft Center following the Apollo-Saturn 204 incident in January 1967 demonstrated that bare or defectively insulated silver-covered copper wires carrying a direct-current potential produced ignition when contacted by glycol/water fluids used in the Apollo environmental control system. Copper, nickel-covered copper, and tin-plated copper wires showed no detectable chemical reactivity and, therefore, no ignition when similarly treated and exposed to glycol/water coolant solutions. Mechanisms of inhibiting glycol/water-induced reactions with metals are discussed with particular reference to the Apollo coolant fluids. Laboratory results indicated that glycol/water fluids, particularly those containing corrosion inhibitors, were extremely difficult to clean from surfaces of wire bundles which had been contaminated by spillages and leakages.

A chemical-reaction mechanism which explains why flammability hazards exist when glycol/water solutions contact silver-wire circuitry carrying direct current is proposed. Measurements of milliamperes current flow during the reaction of glycol/water with silver and utilization of a transistorized amplitude-modulation receiver for detecting radiofrequency emissions are described as a means of locating circuitry defects leading to flammability. Since glycol/water coolant fluids cannot easily be removed from contaminated circuitry, use of a silver chelating agent, benzotriazole, in the glycol/water coolant to arrest chemical reactivity and thereby minimize the hazard of flammability is proposed.

The following conclusions are drawn from this study:

1. Glycol/water solutions cannot effectively be evaporated from a region on which spillage has occurred because the ions contained in the corrosion inhibitors of the fluid remain after evaporation of the low-vapor-pressure-producing glycol.
2. The ionizable amine-containing materials remaining after evaporation of glycol/water coolant fluid from equipment surfaces will absorb moisture from the surroundings, becoming progressively more alkaline as the amines are hydrolyzed by the absorbed moisture.
3. Glycol/water solutions with or without inhibitor additions (except for the addition of benzotriazole) produce flammable reactions accompanied by easily detectable radiofrequency radiation upon contacting silver-covered copper wires on which a direct-current potential is impressed.
4. Pure copper, nickel-covered copper, or tin-plated wires do not show evidence of chemical reactivity towards glycol/water solutions.
5. Silver-covered copper wires in spacecraft circuitry exposed to glycol/water coolant, or likely to be so exposed, should be recognized as a potentially dangerous ignition source in air or in an oxygen atmosphere.
6. If contamination of silver-wire circuitry occurs, rinsing with distilled water until only a nominal ion pickup is indicated in the rinse water constitutes the recommended decontamination procedure for spacecraft.

7. A silver chelating agent, benzotriazole, when added to glycol/water coolant fluids in concentrations from 2000 to 5000 ppm, completely inhibits reactivity of glycol/water solutions to silver wires.

8. A transistorized amplitude-modulation receiver will pick up a constant radio-frequency static noise as the chemical reaction of glycol with silver wire progresses. Such a receiver, therefore, should serve as a ready detector of incipient trouble in wire circuitry during spacecraft tests and checkout.

Manned Spacecraft Center  
National Aeronautics and Space Administration  
Houston, Texas, November 20, 1967  
914-50-20-21-72

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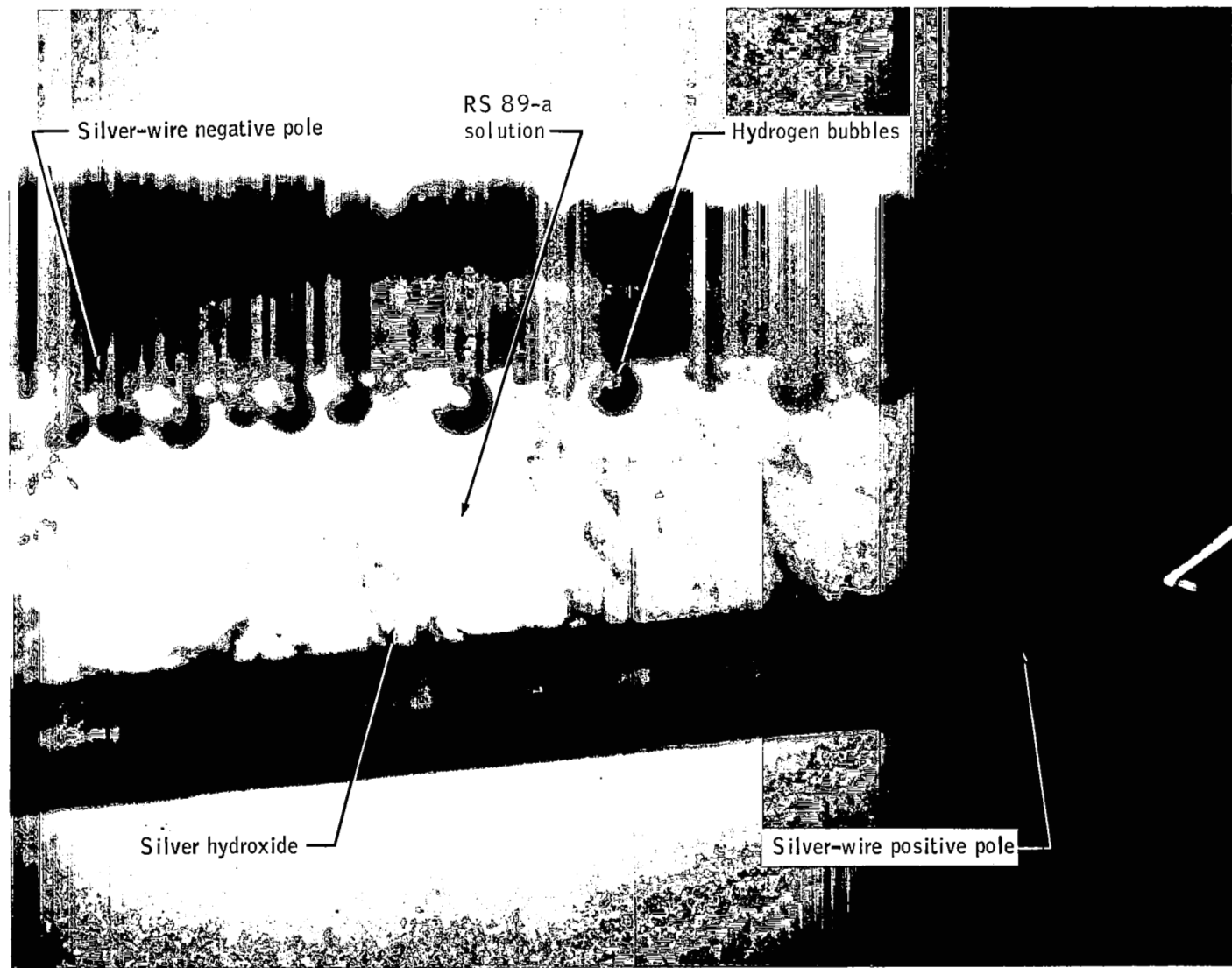


Figure 1. - Photomicrograph showing formation of silver hydroxide and hydrogen when a glycol/water solution first contacts silver-covered copper wires.

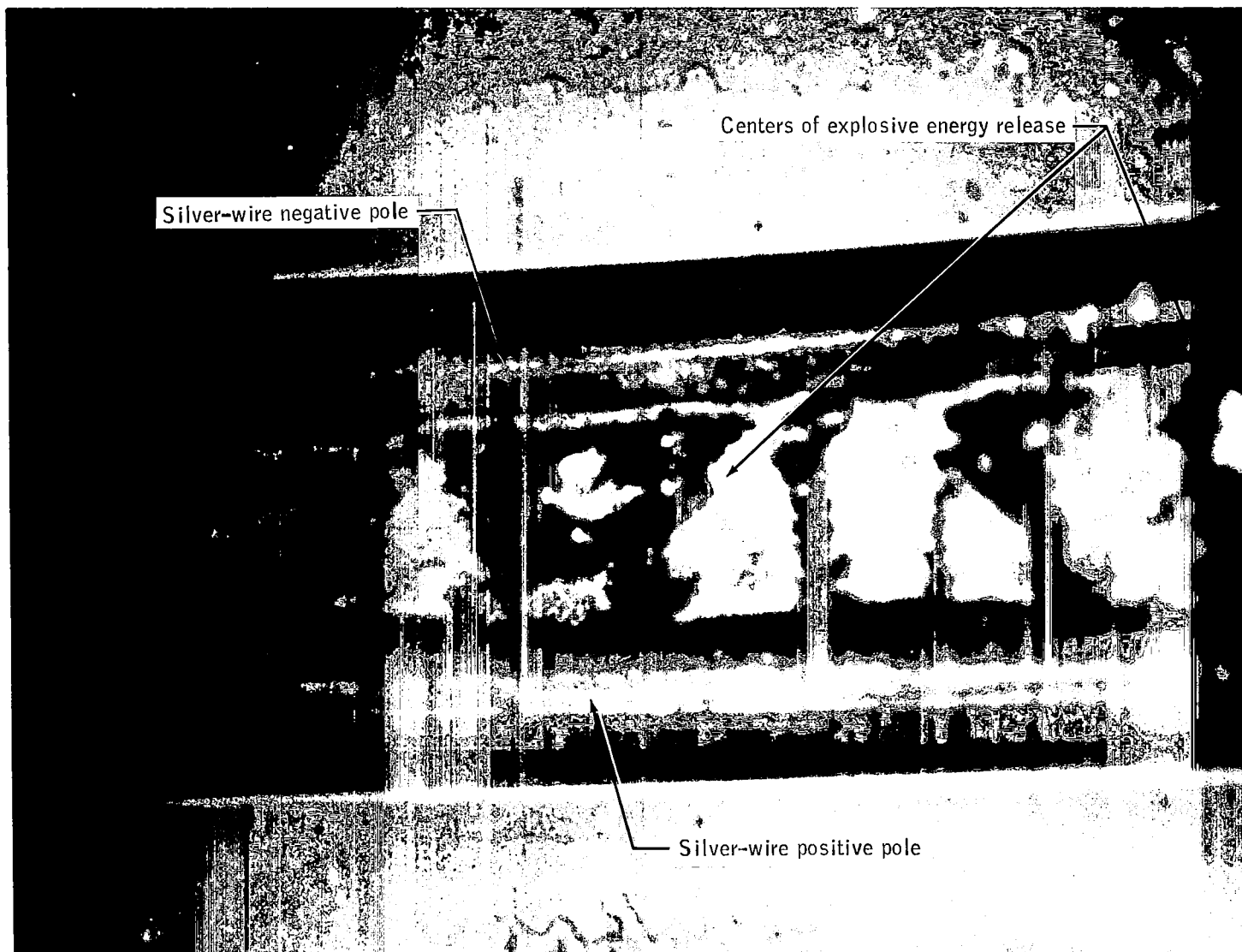


Figure 2. - Photomicrograph showing conglomeration of silver oxide in which centers of explosive energy release can be seen.



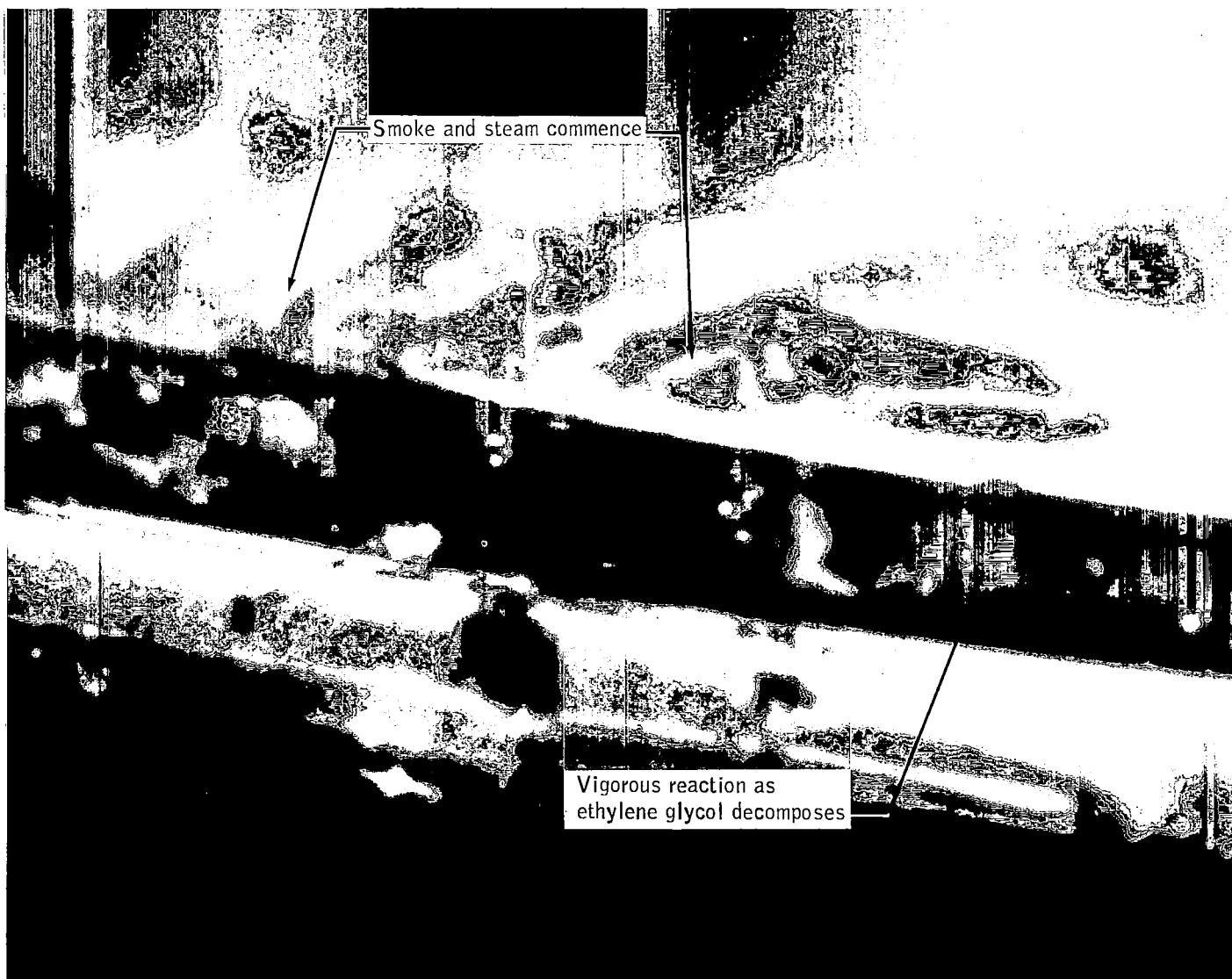


Figure 3. - Photomicrograph showing initiation of smoke and steam and a region of massive dehydration of ethylene glycol to form ethylene oxide and ethylene.



Figure 4. - Photomicrograph showing copious liberation of steam and generalized decomposition of ethylene glycol along the wire surfaces.

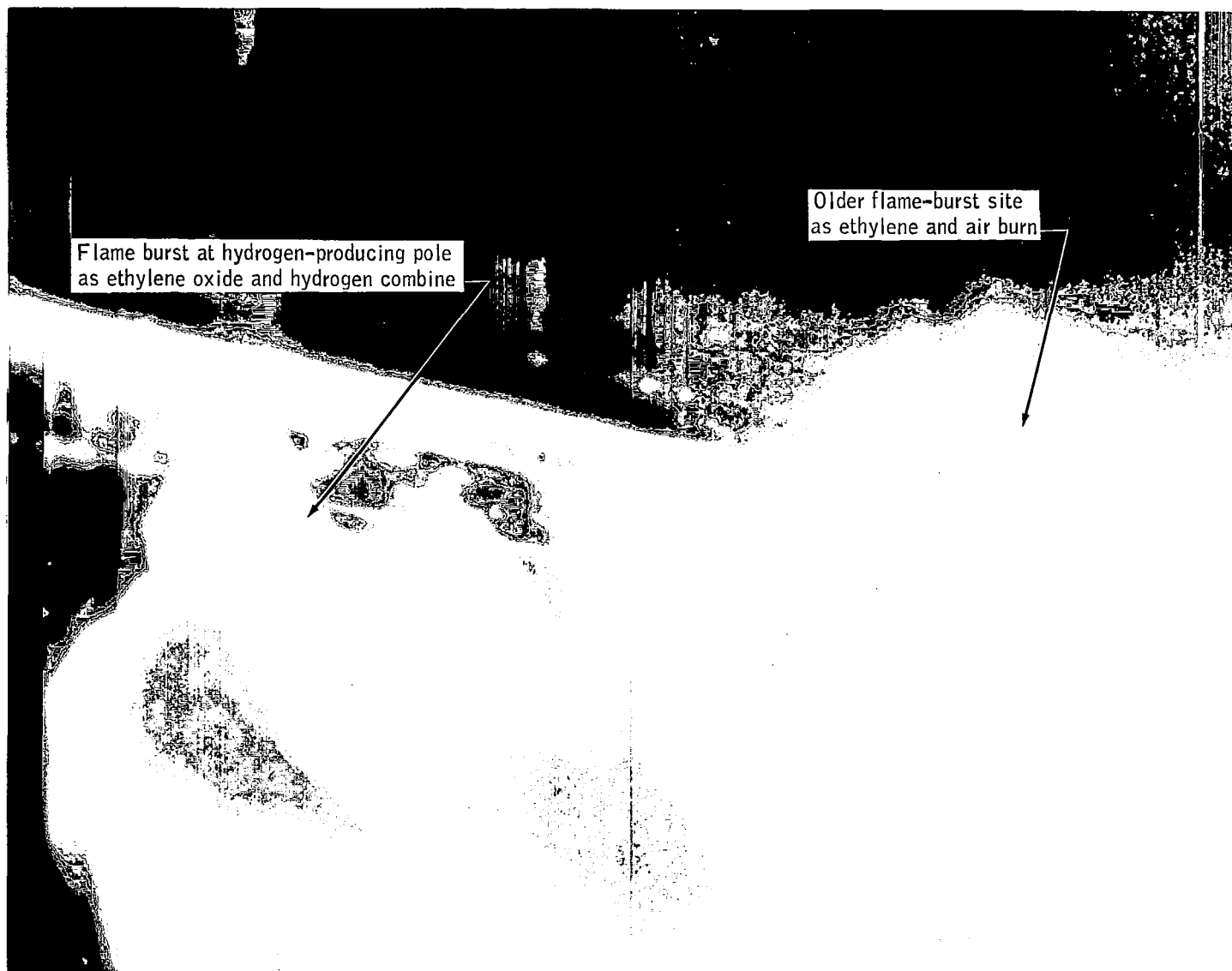


Figure 5. - Photomicrograph showing a burst of flame at the wire surface of the negative pole caused by ignition of ethylene oxide and hydrogen and of ethylene with oxygen of the air.

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